

Searching for low-workfunction phases in the Cs-Te system: the case of Cs₂Te₅

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We have computationally explored workfunction values of Cs₂Te₅, an existing crystalline phase of the Cs-Te system and a small bandgap semiconductor, in order to search for reduced workfunction alternatives of Cs₂Te that preserve the exceptionally high quantum efficiency of the Cs₂Te seasoned photoemissive material. We have found that the Cs₂Te₅(010) surface exhibits a workfunction value of ≈ 1.9 eV when it is covered by Cs atoms. Cs₂Te₅ is analogous to our recently proposed low-workfunction materials, Cs₂TeC₂ and other ternary acetylides [J. Z. Terdik, *et al.*, Phys. Rev. B 86, 035142 (2012)], in as much as it also contains quasi one-dimensional substructures embedded in a Cs-matrix, forming the foundation for anomalous workfunction anisotropy, and low workfunction values. The one-dimensional substructures in Cs₂Te₅ are polytelluride ions in a tetragonal rod packing. Cs₂Te₅ has the advantage of simpler composition and availability as compared to Cs₂TeC₂, however its low workfunction surface is less energetically favored to the other surfaces than in Cs₂TeC₂.

I. INTRODUCTION

Cesium Telluride (Cs₂Te) has been known since the 1950-s as an exceptionally high quantum efficiency photoemissive material¹, it can turn as much as $\approx 20\%$ of the incident ultraviolet photons into emitted electrons². Cesium Telluride also has the advantage of relatively long operational lifetime, 20-30 times longer than that of competing multi-alkali antimonide photocathodes, such as K₂CsSb and (Cs)Na₃KSb. While K₂CsSb and (Cs)Na₃KSb require ultrahigh vacuum for operation, Cs₂Te can operate in orders of magnitudes lower levels of vacuum³. In order to further enhance the photoemissive properties of Cs₂Te for certain applications, modifications are required that decrease its workfunction from the ≈ 3.0 eV down to the visible light spectrum (1.5-3.0 eV) while preserving its high quantum efficiency. Such modifications can lead to, for example, for high brightness electron guns^{3,4}, better pulse shaping of the incident photons in the visible spectrum and eliminating the need for wavelength down-conversion. Wavelength down-conversion is used to convert the typically near-infrared photons of the laser source to ultraviolet wavelength which causes a great loss of the intensity of the initial laser-beam. One possible way to an improved photoemissive material that we recently proposed⁵ is the acetylation of Cs₂Te leading to Cs₂TeC₂, a new member of the existing family of ternary acetylide⁶⁻⁸ compounds. Electronic structure calculations predict that the new Cs₂TeC₂ and other, existing ternary acetylides, such as Cs₂PdC₂ would have similarly high quantum efficiencies as Cs₂Te, but significantly lower, 2.0-2.4 eV workfunctions.

An alternative route to the acetylation in developing improved photoemissive analogues/derivatives of Cs₂Te might be in the exploration of photoemissive properties of other Cs-Te phases. A comprehensive review of alkali tellurides by D. M. Smith and J. A. Ibers⁹ called our attention to Cs₂Te₅, an existing¹⁰ crystalline phase

of Cs and Te. Remarkably, the Te₅²⁻ polytelluride anions in Cs₂Te₅ self organize to ≈ 4 Å wide wavy ribbons of Te with continuous covalent Te-Te networks, which are embedded into a Cs matrix, such as shown in Fig. 1. In the wavy Te-ribbons, six-membered rings of Te in chair-conformation are connected via common vortices into quasi 1D chains, as depicted in Fig. 2. These quasi 1D substructures of Cs₂Te₅ resemble the rod-like polymeric $[-\text{Te}-\text{C}\equiv\text{C}]_n^{2n-}$ substructures that are responsible for the improved photoemissive properties of Cs₂TeC₂. This structural analogy directed our attention towards the computational analysis of Cs₂Te₅ to check whether it can potentially serve as an improvement to Cs₂Te and ternary acetylides.

II. METHODOLOGY

The electronic structure calculations in the present study have been carried out using the Quantum Espresso program package¹¹. The PBE exchange-correlation potential¹² has been used with norm-conserving Cs and Te pseudopotentials identical to those in our study for Cs₂TeC₂ in Ref. 5. The wavefunction-cutoff was 80 Rydbergs. The k-space grids were at least $6\times 6\times 6$ large for optimizations, the residual forces on fractional coordinates were less than 4×10^{-4} Ry/au, residual pressure on the unit cell less than 1 kbar. The application of these pseudopotentials has been validated on known properties (structure and workfunction) of crystalline Cs, Te and Cs₂Te. This method provides $a=9.719$, $b=12.178$ and $c=10.407$ Å for the calculated lattice parameters of Cs₂Te₅, while the experimental ones¹⁰ are $a=9.373$, $b=12.288$ and $c=10.140$ Å, an agreement within 3.5%. There are two different Te-Te bond lengths in Cs₂Te₅: the calculated values are 2.845 and 3.090 Å, the experimental ones are 2.765 and 3.049 Å, respectively, an agreement within 3%. Experimental and calculated lattice angles are all 90°. Optical absorption spectra have

been calculated in the Random Phase Approximation (RPA) as implemented in the YAMBO¹³ code, the spectra were calculated using a gradually increased number of plane waves and interaction block-size until convergence at 20000 plane waves and an interaction block size of 403. For comparison, data for Cs_2Te and Cs_2TeC_2 have been taken from Ref. 5. The workfunction calculations were based on slabs of at least 30 Å width separated by vacuum layers up to 30 Å following the methodology of Ref. 14. Only the top and bottom two layers were relaxed while middle layers were kept at the bulk optimum structures.

The two most important crystal surfaces of Cs_2Te_5 that do not cleave the polytelluride anions and have Miller indices of (010) and (110) have been considered. The cleavage of polytelluride anions is energetically unfavored and would lead to a plethora of possible surface reconstructions. To estimate the strength of the simplest such cleavage, properties of the (001) surface have also been calculated. For the (010) surfaces, two different cleavages have been modeled, (010)-C1 and (010)-

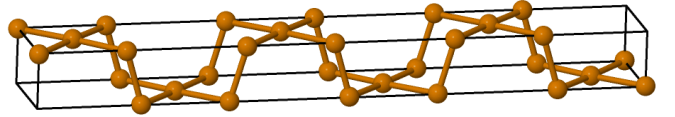


FIG. 2: An isolated Te-ribbon of the 3x3x3 supercell of Cs_2Te_5 . In the wavy Te-ribbons, six-membered rings of Te in chair-conformation are connected via common vortices into quasi 1D chains.

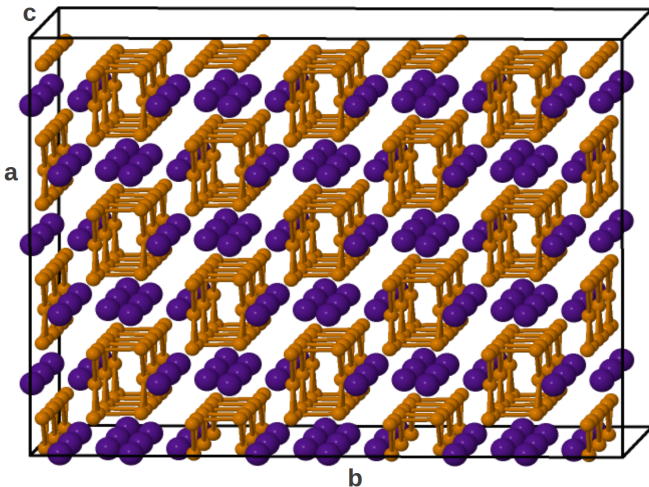


FIG. 1: A near top down view of a 3x3x3 supercell of the rectangular unit cell of Cs_2Te_5 . Cell data are from Ref. 10. Bronze spheres denote Te, blue ones are Cs. Notice the quasi 1D $[\text{Te}_5^{2-}]_n$ polytelluride ions embedded in Cs matrix in the form of ≈ 4 Å wide wavy Te-ribbons, showed in detail in Fig. 2.

C2. The (110) and (010)-C1 surface slabs have identical top and bottom surfaces, while the (010)-C2 surfaces are not identical. The (010)-C1 surface slab leaves some Te atoms directly exposed on both of its surfaces, while the (010)-C2 one has one fully Cs covered surface and one partially Cs covered one.

III. RESULTS AND DISCUSSION

The bandstructure of Cs_2Te_5 is shown in Fig. 3. It indicates a band gap of 0.19 eV, i.e. a small bandgap semiconductor material. The optical absorption spectra of Cs_2Te_5 with different light polarizations are presented in Fig. 4 and are compared to those of Cs_2Te and Cs_2TeC_2 . The small gap value and the strong absorption at low photon energies appears to be consistent with the experimentally observed “metallic grey” color¹⁰ of Cs_2Te_5 . The workfunction values for several important crystallographic surfaces of Cs_2Te_5 are listed in Table I. It is apparent that the lowest workfunction belongs to the Cs_2Te_5 (010)-C2 surface with fully Cs-covered polytelluride ribbons. The other surfaces have much greater

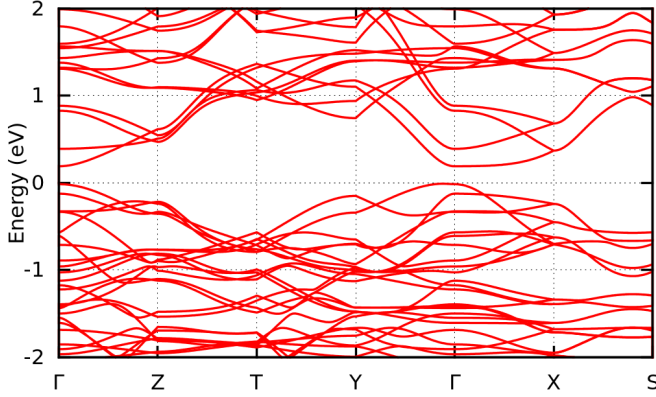


FIG. 3: Band structure of Cs_2Te_5 . Energy levels are relative to the top of the valence band. The band gap is 0.19 eV. The selection of the special k-points is based on the orthorhombic symmetry of the cell and is identical with that used for Cs_2Te in Ref. 5, as both Cs_2Te (space group: Pnma) and Cs_2Te_5 (space group: Cmcm) crystallize in the orthorhombic system.

TABLE I: Calculated properties of Cs_2Te_5 surfaces: workfunctions (Φ), bandgaps at the Γ -point $E_g(\Gamma)$ and surface energies (σ). For the $\text{Cs}_2\text{Te}_5(010)$ -C2 cleavage, data refer to the fully Cs-covered surface. The workfunction of this surface has been calculated both from the asymmetrically Cesiumated $\text{Cs}_2\text{Te}_5(010)$ -C2 slab ($\Phi = 1.87$ eV) and from the symmetrized (with additional Cs) and relaxed version of it ($\Phi = 1.97$ eV). The average surface energy of the asymmetrically Cesiumated $\text{Cs}_2\text{Te}_5(010)$ -C2 slab was $22.6 \text{ meV}/\text{\AA}^2$, the contribution of the Cs-rich side is estimated to be close to the $\text{Cs}_2\text{Te}_5(010)$ -C1 value ($\sigma = 7.1 \text{ meV}/\text{\AA}^2$).

surface	Φ (eV)	$E_g(\Gamma)$ (eV)	σ ($\text{meV}/\text{\AA}^2$)
$\text{Cs}_2\text{Te}_5(110)$	3.22	0.3577	7.2
$\text{Cs}_2\text{Te}_5(010)$ -C1	3.47	0.3344	7.1
$\text{Cs}_2\text{Te}_5(010)$ -C2	1.87/1.97	0.0309	-
$\text{Cs}_2\text{Te}_5(001)$	4.70	0.0369	20.4

workfunctions, in the 3.2-3.5 eV range or even above for the $\text{Cs}_2\text{Te}_5(001)$ cleavage. Also note that cleaving the

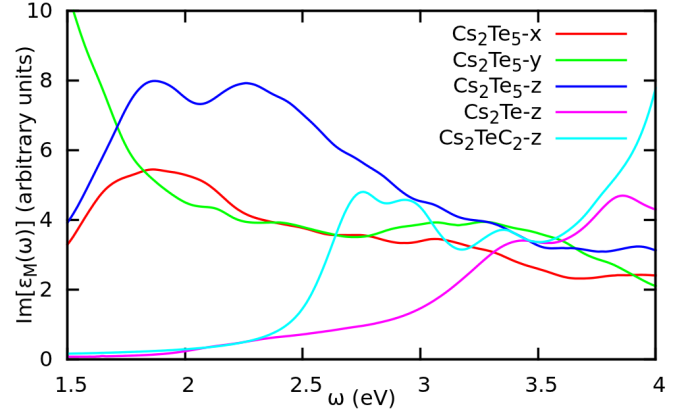


FIG. 4: Optical absorption spectra in terms of the macroscopic dielectric constant $\varepsilon_M(\omega)$ for Cs_2Te_5 as compared to that of Cs_2Te and Cs_2TeC_2 . The energy of the incident photons is denoted by ω , while the polarization of the photons is indicated by the coordinate directions in the curve-keys with z being parallel with the main crystallographic axis. The calculations predict that Cs_2Te_5 would have a significantly higher absorption probability at lower photon energies, also at ≈ 1.9 eV which is the workfunction value of the Cs-covered $\text{Cs}_2\text{Te}_5(010)$ surface.

polytelluride ribbons results in a relatively large surface energy, i.e. it is energetically very unfavorable as compared to the other cleavages.

Comparing the workfunction value of ≈ 1.90 eV for the Cs-rich one of the $\text{Cs}_2\text{Te}_5(010)$ -C2 surfaces to the optical absorption spectra in Fig. 4 one can see a very strong absorption at 1.9 eV. This means that if this surface can be realized, it will have not only a significantly (by more than 1 eV) reduced workfunction, but also an even higher optical absorption than Cs_2Te , and as a consequence its quantum yield may be higher than that of Cs_2Te . At the same time, Cs_2Te_5 is just a two-component material and its synthesis is readily available from the literature¹⁰. It is however also to be noted that the surface energy differences between the (010) and (110) surfaces are very small, making it difficult to realize the Cs-covered $\text{Cs}_2\text{Te}_5(010)$ -C2 cleavage without coexisting presence of other sur-

faces. Since large single crystals can be grown of Cs_2Te_5 as reported in Ref. 10, the suitable cleavage of them could deliver the required surface. Since the Cs_2Te_5 material is relatively soft due to the weak interaction between Te-ribbons and the small cleavage energy between Cs-covered Te-ribbons, it may also be deposited along these easy-to-cleave surfaces by rubbing larger crystals of Cs_2Te_5 to the substrate surface, similarly to deposition of graphite.

Bandgaps of the surface slabs at the Γ -point differ somewhat from the bulk-value (0.19 eV) in the range of ≈ 0.037 -0.360 eV, being smallest for the lowest workfunction $\text{Cs}_2\text{Te}_5(010)$ -C2 slab.

While the acetylated Cs_2Te , i.e. Cs_2TeC_2 , shows very anisotropic workfunction values, surface energies and optical absorptions (a factor of 9 optical absorption differences⁵), the degree of anisotropy is somewhat smaller for Cs_2Te_5 , where optical absorptions may differ by a factor of two in the visible spectral range.

IV. CONCLUSIONS

In the present study we have computationally analyzed bulk and surface properties of Cs_2Te_5 , an existing¹⁰ crys-

talline phase of the Cs-Te system, in order to search for alternatives of Cs_2Te in the Cs-Te system with reduced workfunctions and high quantum efficiency. We have found that the fully Cs-covered $\text{Cs}_2\text{Te}_5(010)$ -C2 surface has a workfunction of ≈ 1.9 eV and a quantum efficiency that is higher than that of Cs_2Te , both at the respective workfunction values. Since large single crystals of Cs_2Te_5 can be produced as described in Ref. 10, this prediction can be validated experimentally, and Cs_2Te_5 can become a practical alternative to Cs_2Te for photophysical applications.

V. ACKNOWLEDGEMENTS

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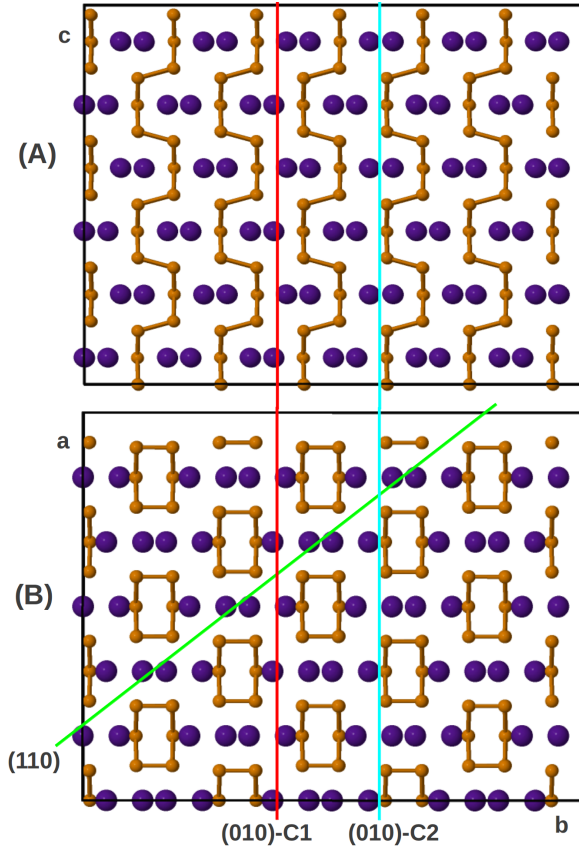


FIG. 5: Panels (A) and (B) show the (bc) and (ba) plane views of a $3 \times 3 \times 3$ supercell of the Cs_2Te_5 crystal, respectively, where a , b and c denote the crystallographic axes. Only those crystal surfaces have been considered that do not cleave polytelluride ions and have small Miller indices. These are (110), (010)-C1 and (010)-C2. The (010)-C1 surface slab leaves some Te atoms directly exposed on both of its surfaces, while the (010)-C2 one has one fully Cs covered surface and one partially Cs covered one.